RAW MATERIALS

BIOCHEMICAL METHOD OF REMOVING IRON FROM ZHURAVLINYI LOG KAOLIN

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The reasons for the inefficacy of iron removal from Zhuravlinyi Log kaolin by dry grading into fractions method are analyzed. A biochemical kaolin-enrichment technology is proposed. Different process regimes and treatment conditions boosting iron reduction and removal from kaolin are studied.

Key words: kaolin, kaolin suspension, color, enrichment, nutrient medium, iron reduction.

Natural kaolin deposits with low coloring impurities content are limited. Different methods for removing coloring impurities from kaolin are used in industry, the best choice giving maximum removal. To find a kaolin enrichment method the coloring impurities must be identified by the mineral composition, dispersity and morphology of the particles.

A domestic source of kaolin products is the Zhuravlinyi Log deposit (ZLD). The color gradation in more than 200 moderately ferruginous and low-ferruginous samples of enriched ZLD kaolin is presented in [1]. It is shown that only a small fraction of the kaolin samples meets the whiteness requirements.

Separating ZLD raw kaolin into fractions during dry enrichment makes it possible to identify on the process filters the kaolin fraction with higher whiteness than that of kaolin samples from cyclones, but small particles (< 2 μm versus $13 – 14$ μm from cyclones) determine the higher whiteness values, which is due to light scattering and, correspondingly, higher lightness with no color change. In dry grading the Fe_2O_3 content is practically the same for all fractions and is determined by its content in the raw kaolin. Iron removal in dry enrichment of ZLD raw kaolin is ineffective mainly because of the microaggregate composition of kaolin and the morphological and structural features of kaolinite. Kaolin microaggregates are represented by kaolinite particles of different sizes right up to superdisperse and x-ray amorphous

with average structural ordering [2]. The iron in ZLD kaolin is located in aggregates with different structural organization, ranging from large crystals to superdisperse particles, probably inside kaolin aggregates or in the form of a cementation phase between the particles of microaggregates. Therefore, to remove iron minerals from kaolin the aggregates must be broken down, which cannot be done in this enrichment method. The low magnetic susceptibility of ZLD kaolin renders magnetic separation methods ineffective [3].

Research on ways to remove weakly magnetic and amorphous iron (hydr)oxides and structural iron from clayey minerals by chemical or biological methods, including different biological and chemical processes, has been done in the last ten years [3, 5 – 11]. In the first variant, portions of the nutrient liquid from bacterial cultures (for example, Bacillus cerens [6, 7]) or fungi (Aspergillus niger [8, 9]) are added; these additions produce organic acids capable of reducing and dissolving (hydr)oxides and forming complexes with the participation of iron compounds. In the second variant, a nutrient medium containing different sources of carbon and nitrogen, promoting the development of a trophic (food) chain of a microbial community in which iron-reducing bacteria perform the main function [3, 5, 10, 11], is introduced into clay and kaolin.

The aim of the present work is to use a complex method of biochemical treatment of ZLD kaolin to remove iron from the kaolin.

A variant of bioactivation of a natural cenosis of microorganisms present in kaolin in a stagnant regime, which is replaced by a flow regime, was chosen on the basis of an analysis of methods for biotreatment of kaolin [12].

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The direction and intensity of biochemical processes during souring of kaolin are determined by a number of necessary and sufficient factors [4]: the moisture content of the kaolin suspension; the presence and composition of microorganisms; the composition and content of the nutrient medium used to grow microflora; and, the temperature – time regime.

The object of this investigation is a product of dry enrichment of the KZHF-2 raw kaolin from ZLD with the following chemical composition (%)[4]: 47.2 SiO_2, 36.50 Al_2O_3, 0.75 Fe_2O_3, 0.30 CaO, 0.15 MgO, 0.03 Na_2O, 0.61 K_2O and 13.80 calcination losses.

The natural microflora of kaolin is represented by aerobic, heterotrophic, denitrifying and iron-reducing bacteria. The presence of fatty acids, whose concentration is 13.1 mg/liter, attests to microbial activity in natural kaolin.

It is well known that the development of microorganisms active in iron reduction or biosynthesis of metabolites largely depends on the nutrient medium used. Chemical substances were used as the nutrient medium for growing microorganisms, the most important being molasses, wastes from processing sugar beets (index M), and a complex inorganic additive (index N) with the nutrient ratios N : P_2O_5 : K_2O = 1 : 1 : 1. The latter contains as the basic components ammonium nitrate NH_4NO_3, ammonium phosphate $(NH_4)_2HPO_4$ and potassium salt.

The additives were introduced in the ratios M : N = 1.5 : 1, but no more than 2.5% of the kaolin mass. As the molasses fraction increases (from 2% or more) during the souring of kaolin the pH of the medium decreases to 5.0 or lower and frothing of the suspension occurs.

A control suspension (with index KO) and two experimental suspensions with indices KM (with addition of molasses) and KMN (with addition of molasses and inorganic substances) were prepared from kaolin (index K) for the experiments. The samples were prepared as follows:

– kaolin was comminuted in a porcelain mortar to a powder, which was placed into a glass container and mixed with distilled water;

– a solution of a nutrient medium was added to the kaolin suspension and the moisture content of the suspension was increased to 60%.

The glass vessels holding the control and experimental suspensions were placed in a thermostat at 30°C for 21 days (souring process).

The soured suspension was placed in a high-gradient CM 15 magnetic separator for magnetic separation.

Two methods were used to remove water from the kaolin suspension washed with a 0.1 M solution of ammonium oxalate: in a gypsum mold to 21 – 23% moisture content and centrifuging in a glass vessel at 8000 rpm.

The following criteria were used to monitor the biochemical processes in the kaolin suspension during and after souring: chemical, based on the ratio of the forms of the iron

compounds; oxidation-reduction state of the suspension medium; post-treatment color characteristics of samples of the suspensions and kaolin.

The chemical composition of kaolin, including the total iron content Fe_{tot} in terms of oxides, was determined with an SMR-25 x-ray fluorescence spectrometer. Parallel determination of oxalate dissolved iron Fe_{oxa} (by means of Tamm's reagent — a mixture of oxalic acid 0.14 M $H_2C_2O_4$ and ammonium oxalate) and dithionitrate dissolved iron Fe_{dit} — dithionitrate-bicarbonate solution (by the Jackson measure method [13]) was used for diagnostics of iron present in kaolin and its structural state. The iron content in the dissolved form Fe_{dis} in a suspension medium was determined spectrometrically.

A pH-150 M pH-meter with an electrode set was used to measure the pH and Eh of a kaolin suspension with the natural moisture content in the inner levels of the vessel.

The values of Eh expressed in millivolts (mV) characterize the flow of redox reactions. The computed quantity, showing the electron activity pe, was determined from the equation [4]

$$pe = Eh : 58.$$

In addition, a combined redox potential rH, taking account of the proton activity pH and the electron activity pe, was used in the present work to evaluate the oxidation-reduction state of the suspension medium

$$rH = 2(pe + pH).$$

The reflection spectra of a kaolin suspension and kaolin were measured with a Pul'sar spectrometer. The color characteristics were determined in the CIE $L^*a^*b^*$ color space. Two axes characterize color: a^* — red ($+a^*$) and green ($-a^*$); b^* — yellow ($+b^*$) and blue ($-b^*$). The third axis, which is perpendicular to the color plane ($a^* - b^*$), determines the lightness L (from 0 to 100).

The relation [1]

$$G = [(1.28X - 1.06Z)/Y] \times 100,$$

where X, Y and Z are the CIE 1931 color space coordinates, was used to evaluate the yellowness G (ASTM E 313).

Gleying of Kaolin Suspensions in a Stagnant Moisture Regime. Gleying can be defined as a redox process of anaerobic destruction of organic substances combined with the reduction of Fe(III) as an electron acceptor. Iron (hydr)oxides and iron-containing silicates acting as electron acceptors significantly accelerate the oxidation of organic substances.

During the period of souring of the control KO and experimental KM suspensions the pH decreases from 8.1 to 6.9 and from 7.8 to 5.5, respectively. On the first day the pH of the experimental suspension KMN decreases, but then gradually increases from 6.3 to 6.9.

For the experimental suspensions Eh decreases in the following order: KO — from 200 to 28, KM — from 144 to –58

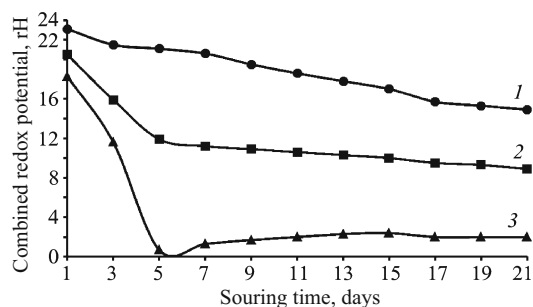[4] Here and below, content by weight, wt.%.

Fig. 1. Variation of the combined redox potential rH of the control and experimental kaolin suspensions versus the souring time of the sample: *1*) KO, *2*) KM, and *3*) KMN.

TABLE 1. Post-Biotreatment Color Characteristics of Kaolin

Sample	Color coordinates				Yellowness G, %
	L^*	a^*	b^*	H	
On the 21st day of souring					
KO	71.4	–1.0	12.7	94.6	28.3
KMN	44.4	–2.3	–1.0	203.5	–6.7
After water removal in a gypsum mold and drying at 18 – 23°C					
KO	84.4	–1.4	11.9	96.8	23.2
KMN	86.2	–2.0	7.4	105.0	13.6
After heat-treatment at 110°C					
KO	91.8	–0.2	9.7	91.0	18.7
KMN	93.1	–0.8	5.9	97.8	11.1
After water removal in a centrifuge and heat-treatment at 110°C					
KO	93.1	–0.3	7.9	92.4	15.0
KMN	94.4	–1.0	4.1	104.4	7.3
After heat-treatment at 475°C					
KO	89.8	1.6	8.8	79.5	18.9
KMN	87.9	0.1	5.1	88.5	10.9

and KMN — from 167 to –340 mV. Converting the Eh values to the redox potential *pe* gave the following range of values for different suspensions: KO — from 3.4 to 0.5, KM — from 2.4 to –1.0 and KMN — from 2.8 to –5.8.

The redox state of the kaolin suspensions varied as follows, according to the gradation of the *pe* values [4], during the souring period:

– on the first day the state corresponded to moderately reduced for all three suspensions; for the control suspension KO it remained so up to 9 days;

– on the third day the state of the experimental suspensions KM and KMN and on the 11th day that of the control KM changed to reduced;

– on the seventh day the state of the experimental KMN suspension changed from reduced to strongly reduced.

Therefore, during the souring period reduction processes dominate in the control (KO) and experimental (KM) suspensions and processes right up to strongly reducing dominate in the experimental suspension KMN.

According to the values of the combined redox potential rH, when a complex inorganic addition (KMN index), which includes nitrogen, phosphorus and potassium compounds, is added in addition to molasses (KM suspension) to the control suspension (suspension KO), the intensity of the redox processes (during souring) increases sharply (see Fig. 1).

A visual comparison of the soured suspensions showed that the color of the experimental suspensions changed compared with the control suspension from light yellow to dark blue-green. The color characteristics of the kaolin suspension KMN in the CIE $L^*a^*b^*$ system confirm the visual observation: the lightness L^* values of the experimental suspension decreased from 71.4 (white) to 44.4 (grey); the color values a^* decreased from –1.0 (red) to –2.3 (green) and b^* from 12.7 (yellow) to –1.0 (blue). Correspondingly, the color hue H^* changed from yellow-green to blue-green (from 93.0 to 203.0) and the yellowness G decreased with a change of sign: from positive +28.5 (yellow) to negative –6.7 (blue) (Table 1).

It is known that the color change of kaolin from light yellow to blue green is due to, first and foremost, the reduction

of iron Fe(III) → Fe(II), which attests to gley formation during the souring period of ceramic pastes [3, 4, 13].

According to modern research the gley formation process was regarded not only as a chemical but also a biological process [4, 5, 13]. On the one hand the bacteria ferment organic substances and form low-molecular organic compounds, which reduce Fe(III), while on the other hand a group of anaerobic bacteria (so-called dissimulatory iron-reducing bacteria [5, 14]) capable of direct reduction of Fe(III) minerals has been discovered recently.

Thus, the study of the oxidation-reduction state and color characteristics of a kaolin suspension in the course of souring in a stagnant regime shows that, firstly, the change of the redox potential of the kaolin suspension from moderately reduced to reduced without the introduction of a nutrient medium is not enough for gley formation to occur and, secondly, a complex additive, including molasses and compounds of nitrogen, phosphorus and potassium, is closest to being optimal for trophic relations to develop in the community of microorganisms and for gley formation to occur.

Structural-Phase Changes of Iron-Containing Impurities During Gley Formation in a Kaolin Suspension. After the kaolin was allowed to sour Shvertman's chemical criterion was determined. This is the ratio of the oxalate dissolved iron Fe_{oxa} to the dithionitrate dissolved iron Fe_{dit} in the kaolin for the parallel extraction scheme: $K_{sh} = Fe_{oxa} : Fe_{dit}$ [2]. In the control sample $K_{sh} = 0.4$, while in the experimental sample it increased to 1.4 (Table 2).

Treatment of samples with the Jackson measure reagent gives a value of Fe_{dit} that can be interpreted as the amount of iron in all nonsilicate compounds (in the form of iron minerals). Tamm's reagent strongly dissolves not only amorphous iron compounds but also different weakly crystallized iron

TABLE 2. Pre- and Post-Biotreatment Physical-Chemical Indicators for Zhuravlinyi Log Kaolin

Sample index	Iron content, wt.%			Specific magnetic susceptibility χ, 10^{-8} m^3/kg (after heating)	
	Fe_{tot}	Fe_{oxa}	Fe_{dit}	110°C	475°C
K	0.78	0.014	0.031	4.2	5.7
KO	0.73	0.019	0.051	0.2	2.9
KMN	0.67	0.031	0.022	0.4	0.9

TABLE 3. Content of Total and Dissolved Iron in the Water Extracts from the Control and Experimental Kaolin Suspensions

Sample index	Before washing		One washing		Two washings	
	Fe_{tot}, mg/liter	Fe_{dis}, mg/liter	Fe_{tot}, mg/liter	Fe_{dis}, mg/liter	Fe_{tot}, mg/liter	Fe_{dis}, mg/liter
KO	0.4	0.2	0.4	0.4	0.5	0.5
KMN	6.0	0.6	7.2	6.6	12.5	12.2

hydroxides Fe_{oxa} as well as magnetite crystals. It is believed that Tamm's reagent dissolves amorphous and weakly crystallized particles by reduction as well as via complex formation by oxalate and in part via protonation.

The increase of the ratio $K_{sh} = Fe_{oxa} : Fe_{dit} > 1$ in gleyified kaolins cannot be attributed to an increase of the amorphous compounds fraction above the nonsilicate iron content. In [13] it is shown that in a stagnation moisture regime it is precisely the amorphous Fe(III) compounds that are reduced but this contradicts the increase in the ratio $K_{sh} > 1$. The real reason lies in the high sensitivity of oxalate to the presence of Fe(II). In the case where a large amount of Fe(II) accumulates during gley formation in a kaolin suspension, the Fe_{oxa} extraction capacity of Tamm's reagent turns out to be higher than the Fe_{dit} extraction capacity of the Jackson measure reagent. The increase in the values of this criterion $K_{sh} = Fe_{oxa} : Fe_{dit} > 1$ in gleified kaolins is explained by two mechanisms: on the one hand the high sensitivity of Tamm's reagent to the presence of Fe(II), which catalyzes the dissolution of Fe(III) – (hydr)oxides, and on the other hand the inhibiting effect of Fe(II) sorbed on the surface of iron particles, which preserves a significant amount of weakly crystallized iron (hydr)oxide particles under the anaerobic conditions of a stagnant moisture regime. This makes it necessary to include a washing regime in the technological scheme for removing iron from kaolin.

Thus, Shvertman's criterion K_{sh} can serve as a diagnostics indicator for chemical and biogenic iron excess during gley formation in kaolin in a stagnant moisture regime. The mechanisms of these processes in a stagnant moisture regime can be represented in the form of the following scheme: formation of anaerobic conditions in the medium → biological

and chemical reduction Fe(III) → Fe(II) → formation of Fe–L complexes → sorption of Fe(II) iron (hydr)oxides → stopping of iron (hydr)oxide reduction → high Fe_{oxa} content.

Therefore, biological reduction of Fe(III) must be added to the known chemical mechanisms resulting in the breakdown of Fe-containing minerals — reduction, acid hydrolysis and complex formation with the participation of ligands. During gley formation in a kaolin suspension with a strongly reduced or reduced medium with pH = 5.5 – 6.5 the Fe-containing minerals dissolve by different mechanisms and their contribution, in general, follows the following order: reduction > complex formation > protonation. The effect of a cenosis of bacteria does not change the sequence but only increases the contribution of reduction compared with other mechanisms for the dissolution of Fe-containing minerals.

In the past it was assumed that Fe(III) reduction is limited only by iron in (hydr)oxides. However, it was established recently [15] that Fe(III) in layered silicates is also captured by microbiological reduction. As a result of Fe(III) reduction in the structure of silicate either iron is removed from silicate particles or they undergo reductive decomposition. But, the least ordered and finely dispersed Fe-containing minerals, irrespective of their form, are subjected to reduction first. Therefore, the loss of both free Fe_{dit} and silicate iron can be expected to occur during gley formation in a kaolin suspension.

Washing Regime of Kaolin Treatment and Water Removal Method. After the suspension soured the kaolin was washed twice with a 0.1 M solution of ammonium oxalate after which the total iron Fe_{tot} and the dissolved iron Fe_{dis} in the washing solution were determined.

After the first and second washings both Fe_{tot} and Fe_{dis} increased in the water extract of the experimental sample as compared with the control sample (Table 3). This is due to different parallel processes of the transformation of iron compounds. On the one hand an increase of Fe_{tot} in the experimental suspension KMN shows that during souring, probably because of the destruction of the cementing phase between particles of kaolinite, iron Fe_{tot} mineral particles are released from the microaggregates, which are predominantly soluble in Tamm's reagent Fe_{dis}. On the other hand in the washing regime of the kaolin treatment the presence of organic ligands L in the water medium promotes the formation of Fe(II)–L complexes followed by their removal from the gleified kaolins. The equilibrium between the dissolved Fe(II) and Fe(II) sorbed on the surface of kaolinite shifts so that the inhibiting effect of Fe(II) sorption decreases. The removal of Fe(II) in the washing regime of kaolin treatment promotes the removal of iron from kaolin.

An important technological stage of iron removal is the separation of the suspension into liquid and solid phases. When water is removed from a kaolin suspension in gypsum molds or filter presses a thin yellow layer forms in the outer layer of the kaolin, which attests to migration of iron compounds together with the water medium and their accumula-

tion in the outer layer. When water was removed from kaolin suspensions by centrifuging, as compared with water removal in gypsum molds, an advantage was gained in the experimental samples (KMN) with respect to the color characteristics: lower yellowness G (7.3 versus 11.1) and higher lightness L^* (94.4 versus 93.1) with color saturation S decreasing (4.1 versus 6.0) (Table 1).

Post-Biotreatment Color Characteristics of Kaolin and the Structural-Phase State of Iron Impurities. The color indicators for KO and KMN samples after heat-treatment at 110 and 475°C are presented in Table 1. The color difference ΔE ($L^*a^*b^*$) [1] between these samples after heat treatment at 110°C is 4.1, and it is determined mainly by the color difference $\Delta a^* = 0.6$ and $\Delta b^* = 3.8$. The coloring power POW F of the iron compounds in KMN kaolin is 52.6% relative to the corresponding values of KO kaolin. Analysis of kaolin samples after heat-treatment at 110 and 475°C showed considerable changes in the specific magnetic susceptibility χ of the experimental samples compared with the control. Thus, if χ of the KMN experimental kaolin sample after drying and heat-treatment at 475°C has its minimum value and varies in the range $0.4 - 0.9 \times 10^{-8}$ m³/kg, then after heat-treatment at 475°C of the KO control sample χ increases from 0.2 to 2.9×10^{-8} m³/kg.

Analysis of the values of the color coordinates a^* and b^* of the kaolin samples after drying at 110°C and heat-treatment at 475°C as compared with the values of the specific magnetic susceptibility shows that the values of a^* and the yellowness b^* of all three samples increase but χ increases only for the control sample, in contrast to the experimental samples KMN (see Tables 1, 2).

The color characteristics of kaolin and kaolin suspension depend on the color hue and the coloring power of iron (hydr)oxide and their ratios. When hematite dominates in kaolin the redness a^* predominates while for high yellowness b^* iron hydroxides predominate.

Therefore, when kaolin is dried after souring the oxidation process Fe(II) → Fe(III) occurs and iron hydroxides are formed, since the values of the yellowness b^* dominate while after heat-treatment at 475°C iron oxides form. But, the specific magnetic susceptibility χ of the KMN experimental samples does not increase, which attests to the state of iron: either magnetically dilute state Fe–O–Si, Fe–O–Al or a cluster associate state or superparamagnetic state Fe–O–Fe.

Several groups of ligands can be identified in the EPR spectrum before and after bio-treatment:

– a number of narrow, strong lines near $g \sim 2.0$, which are formed by at least three different electron-hole centers (not discussed here);

– a very weak, wide signal near $g \sim 2.0 - 3.0$ associated with crystallized mineral particles of iron hydr(oxides); since the intensity of this weak signal remains practically unchanged after biotreatment as compared with the control sample, it can be supposed that their fraction with respect to

total iron content is very low (probably, most of the iron impurities are in a superparamagnetic state);

– strong signals in a weak paramagnetic field near $g \sim 4.0$ ("structural" iron), recorded in the form of a triplet; they are usually interpreted as a superposition of the spectra of two centers: Fe(I) — with central line $g \sim 4.27$; Fe(II) center — with $g = 4.9, 3.7$ and 3.5; there is no opinion regarding the structural position of Fe^{3+} in kaolinite, but experimental studies show that the intensity ratio of the signals of two centers — Fe(I) and Fe(II) — is related with the degree of ordering of the kaolinite structure and specific surface area; according to [2] the relation Fe(I) > Fe(II) holds for ZLD kaolin, indicating that the kaolinite structure is disordered and highly disperse with a large specific surface area; after biotreatment the strength of the $g \sim 4.9$ signal of kaolinite increases more than that of the signal at $g \sim 4.9$, and therefore the gley formation process in the kaolin suspension increases the ratio Fe(I) > Fe(II) and, correspondingly, the fraction of fine and superdisperse particles; thus, it can be assumed that disaggregation of kaolin particles occurs during the gley formation process.

The rate of bacterial reduction of Fe(III) during gley formation depends weakly on the thermodynamic properties of iron minerals and strongly on their specific surface area (on the density of reactive sites on the surface). Owing to its physical-chemical surface activity kaolinite with average ordering promotes the formation of weakly crystallized and highly disperse crystals of iron (hydr)oxides. Iron is also present in aluminum silica gels, but it is distributed not chaotically but rather in highly disperse clusters of (hydr)oxides. For this reason, during gley formation iron reduction occurs above all in film iron adsorbed on the surface of kaolinite particles and in iron-containing aluminum silicon gels, which cement kaolinite particles, compared with crystallized particles of iron minerals with relatively lower specific activity. These results agree well with previous studies of the whitening of kaolin [16]. The use of Mössbauer spectroscopy to explain the removal of iron compounds from kaolin with different structural organization showed that it is more effective to use oxalic acid to remove film iron from the surface of kaolinite than a dithionate solution, though the latter, combined with subsequent centrifugal separation to remove the washing solution, is more often used to whiten kaolin.

In summary, biotreatment and washing result in iron reduction and removal of iron with structural iron Fe(III) increasing from the total iron content in kaolin.

Conclusions. The reasons the iron removal from ZLD kaolin by conventional methods — magnetic separation and grading of kaolin according to fractions — are ineffective were analyzed. To remove iron minerals from kaolin aggregates of kaolinite particles must be broken up during the enrichment process.

A technology for biochemical treatment of kaolin with the following stages was proposed to remove iron: picking a nutrient medium for growing microflora; determining the

conditions and regime for souring kaolin in a stagnant water regime; and, picking a washing solution and method for removing water from the kaolin suspension.

A nutrient medium, which includes a complex consisting of molasses and compounds of nitrogen, phosphorus and potassium, was used to cultivate natural microflora and to develop gley formation in a souring kaolin suspension.

The development of natural microflora and gley formation in a stagnant souring regime results in, firstly, Fe reduction predominately in x-ray amorphous and weakly crystallized particles of (hydr)oxides on the surface of kaolinite and Si–Al–Fe gels, cementing particles of kaolinite, which promotes the breakdown of kaolinite microaggregates and release of iron (hydr)oxide particles from them and, secondly, a washing regime with ammonium oxalate protonation, reduction and formation of Fe–L (ligands) complexes removed with the washing solution during centrifugal separation.

The biotreatment of kaolin results in, firstly, a decrease of the coloring power of iron compounds as a result of their partial removal and, secondly, improvement of its color characteristics — the yellowness b^* and redness a^* decrease with increasing lightness L^*.

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